methyl was 1/4; the ratio of ketone methyl to cyclobutene methylene was 1/1.5. The crude mixture was heated for 1 hr. on a steam-bath; the n.m.r. spectrum showed that the peaks at 8.0 and 0.4 τ (XV) were greatly enhanced at the expense of the peaks between 5.23–7.4 τ (XVI). However, some new broad peaks did appear in the latter region. In this spectrum the ratio of the area of the phenyl hydrogens to ketone methyl was 15.4/1. The ratio of aldehyde methyl to ketone methyl was 1/1. The ultraviolet spectrum showed shoulders at 275 (3.72) and 250 mμ (3.95).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON, SEATTLE, WASH.]

The Chromic Acid Oxidation of Aromatic Aldehydes. Some Observations Concerning the Oxidation by the Chromium Species of Intermediate Valence[1]

BY KENNETH B. WIBERG AND WILLIAM H. RICHARDSON

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The effect of substituents and the kinetic isotope effect for the oxidation of benzaldehyde by the chromium species of intermediate valence has been determined by a competition technique. The oxidation of triphenylacetaldehyde has been found to give triphenylacetic acid, triphenylcarbinol and carbon monoxide as the main products. The significance of the results is discussed in terms of the possible mechanisms for the reaction.

The first step in many chromic acid oxidations appears to involve a two-electron transfer giving chromium(IV).[2] The chromium(IV) may either react with chromium(VI) to give two chromium(V), or it may react with the organic substrate to give chromium(III) and a free radical. The latter would probably react with chromium(VI) to give the oxidized organic species and chromium(V), which would in turn effect further oxidation.[3] In either case, two-thirds of the net reaction will proceed *via* oxidation by the chromium species of intermediate valence, and one one-third involves chromium(VI).

Even if the initial step were a one-electron oxidation, the above conclusion would apply. Such a reaction would lead to chromium(V) which would effect a net two-electron oxidation. The various possibilities may be represented as follows, where AH_2 is the compound being oxidized.

$$\text{(A)}\quad AH_2 + Cr^6 \longrightarrow A + 2H^+ + Cr^4$$
$$Cr^4 + Cr^6 \longrightarrow 2Cr^5$$
$$2(AH_2 + Cr^5 \longrightarrow A + 2H^+ + Cr^3)^4$$
$$\text{(B)}\quad AH_2 + Cr^6 \longrightarrow A + 2H^+ + Cr^4$$
$$AH_2 + Cr^4 \longrightarrow AH\cdot + H^+ + Cr^3$$
$$AH\cdot + Cr^6 \longrightarrow A + H^+ + Cr^5$$
$$AH_2 + Cr^5 \longrightarrow A + 2H^+ + Cr^3$$
$$\text{(C)}\quad AH_2 + Cr^6 \longrightarrow AH\cdot + H^+ + Cr^5$$
$$AH\cdot + Cr^6 \longrightarrow A + 2H^+ + Cr^5$$
$$2(AH_2 + Cr^5 \longrightarrow A + 2H^+ + Cr^3)$$

Although much is known about the oxidation of organic compounds by chromium(VI), little is known about the stoichiometrically more important oxidation by the chromium species of intermediate valence. From the limited data presently available, it appears that chromium(V) may behave differently from chromium(VI). For example, whereas phenyl-*t*-butylcarbinol is oxidized to the ketone with chromium(VI), the oxidation by the chromium species of intermediate valence gives, under certain conditions, only cleavage to benzaldehyde and *t*-butyl alcohol.[5]

It is not possible to study the oxidation by chromium(IV) and -(V) directly since these species are not stable under the reaction conditions. It is, however, possible to obtain some information concerning their mode of action by studying oxidations of mixtures of organic substrates. Consider the oxidation of a mixture of benzaldehyde and *p*-chlorobenzaldehyde using chromic acid. The chromic acid will react with the two aldehydes in the ratio of the relative reactivities determined in separate kinetic runs. This initial step will lead to the formation of chromium(IV) and -(V), either one or both of which may react further with the aldehydes with the relative reactivity characteristic of that reagent. Thus, having the relative reactivity determined by competition experiments, and correcting this for the known relative reactivity toward chromium(VI), one may obtain the relative reactivity toward the chromium species of intermediate valence.

Competitive oxidations were carried out using several pairs of aldehydes labeled with carbon-14. Aliquots of the reaction mixture were removed and quenched at reasonable intervals, and known amounts of unlabeled aldehydes were added. The aldehydes were isolated and were separated by vapor phase chromatography. They were then converted to the corresponding benzoic acids, purified further by recrystallization, and analyzed for their carbon-14 content. The data for the competitive oxidation of benzaldehyde and *p*-chlorobenzaldehyde are given in Table I.

It is reasonable to assume that the oxidation of benzaldehyde by chromic acid involves an initial two-electron step. Whereas the rate of oxidation of hydrocarbons[6] and of diisopropyl ether,[7] which presumably involves a hydrogen abstraction, is proportional to the concentrations of both the acid

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[1] This investigation was supported by the U. S. Atomic Energy Commission.

[2] W. Watanabe and F. H. Westheimer, *J. Chem. Phys.*, **17**, 61 (1949); F. H. Westheimer, *Chem. Revs.*, **45**, 419 (1949).

[3] A reaction leading to chromium(II) is also possible, but somewhat unlikely in view of the strong reducing properties of this species.

[4] For this sequence, it has been noted[3] that if chromium(V) reacted by one-electron step, the reaction would be autocatalytic. Similar arguments may be advanced for sequences B and C. This type of behavior has not been observed.

[5] J. Hampton, A. Leo and F. H. Westheimer, *J. Am. Chem. Soc.*, **78**, 306 (1956).

[6] K. B. Wiberg and R. J. Evans, *Tetrahedron*, **8**, 313 (1960).

[7] R. Brownell, A. Leo, Y. W. Chang and F. H. Westheimer, *J. Am. Chem. Soc.*, **82**, 406 (1960).

TABLE I

COMPETITIVE OXIDATION OF BENZALDEHYDE AND *p*-CHLOROBENZALDEHYDE[a]

Aliquot	Time, min.	Benzaldehyde added, g.	*p*-Chloro-benzaldehyde added, g.
1	10.9	1.9625	1.8189
2	27.7	2.0200	1.9778
3	43.0	2.0315	1.8300

Sample[b]	Spec. act. of benzoic acids, μc./g.	Concn. of aldehydes × 10^2
A_1	0.0421	1.65
B_1	.0173	1.49
A_2	.0314	1.25
B_2	.0121	1.12
A_3	.0273	1.09
B_3	.00984	0.834

[a] $[C_6H_5CHO] = 0.025$ *M*, 0.860 μc./g.; $[p\text{-}ClC_6H_4CHO] = 0.025$ *M*, 0.286 μc./g.; $[Cr^6] = 0.0337$ *M*, $[HClO_4] = 0.204$ *M*; $[Mg(ClO_4)_2] = 0.065$ *M*, $T = 30.0°$, 91% HOAc. [b] A refers to benzoic acid, B refers to *p*-chlorobenzoic acid, and the subscripts refer to the aliquot number.

chromate and dichromate ions, the rate of oxidation of benzaldehyde[8] and of secondary alcohols[9] is proportional only to the concentration of the acid chromate ion. The dissimilarity between the oxidation of hydrocarbons and aldehydes, coupled with the similarity between the oxidation of aldehydes and alcohols (which have been shown to involve a two-electron oxidation[2]) supports our assumption. The effect of substituents on the oxidation of aromatic aldehydes also is in accord with an initial two-electron oxidation.[8]

For convenience in the discussion, the following mechanism will temporarily be assumed. Here A and B are the two aldehydes, S is chromium(VI), T is chromium(V), U is chromium(IV), and P is the product of the reaction.

$$\mathrm{A} + \mathrm{S} \xrightarrow{k_1} \mathrm{P} + \mathrm{U}$$

$$\mathrm{B} + \mathrm{S} \xrightarrow{k_2} \mathrm{P} + \mathrm{U}$$

$$\mathrm{U} + \mathrm{S} \xrightarrow{k_3} 2\mathrm{T}$$

$$\mathrm{A} + \mathrm{T} \xrightarrow{k_4} \mathrm{P}$$

$$\mathrm{B} + \mathrm{T} \xrightarrow{k_5} \mathrm{P}$$

The appropriate kinetic equations are

$$\mathrm{d}A/\mathrm{d}t = -k_1AS - k_4AT$$

$$\mathrm{d}B/\mathrm{d}t = -k_2BS - k_5BT$$

$$\mathrm{d}U/\mathrm{d}t = k_1AS + k_2BS - k_3US$$

$$\mathrm{d}T/\mathrm{d}t = 2k_3US - k_4AT - k_5BT$$

Applying the steady state approximation, we may set the last two equations equal to zero giving

$$T = 2S\left[\frac{k_1\mathrm{A} + k_2\mathrm{B}}{k_4\mathrm{A} + k_5\mathrm{B}}\right]$$

Starting with equal concentrations of A and B, this becomes at time zero

$$T = 2S\left[\frac{k_1 + k_2}{k_4 + k_5}\right]$$

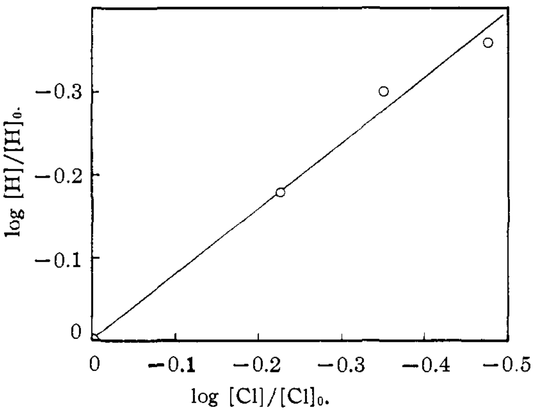

Fig. 1.—Competitive oxidation of benzaldehyde and *p*-chlorobenzaldehyde.

and making this substitution into the equations for the rate of disappearance of A and of B, we obtain

$$\frac{\mathrm{d}A}{A} = \frac{\mathrm{d}B}{B}\left[\frac{3k_1k_4 + k_1k_5 + 2k_2k_4}{3k_2k_5 + k_2k_4 + 2k_1k_5}\right]$$

If we call $k_1/k_2 = R_1$ and $k_5/k_4 = R_2$, and integrate the expression, this gives

$$\log\frac{A_t}{A_0} = \log\frac{B_t}{B_0}\left[\frac{3R_1 + R_1R_2 + 2}{3R_2 + 2R_1R_2 + 1}\right]$$

A plot of log A_t/A_0 against log B_t/B_0 for given values of *t* will produce a curve (or in favorable cases where the concentrations of A and B stay approximately equal, a straight line) for which the tangent at zero time will be equal to the bracketed quantity. Even though the value of *T* which was introduced was correct only at zero time, this gives the correct result since it is based on the changes near zero time.

Figure 1 shows a plot of this type for the data given in Table I. The relationship appears to be close to linear, and the slope is 1.26. The relative rate of reaction toward chromium(VI) was 1.38,[8] thus giving $R_2 = 0.83$, or $k_4/k_5 = 1.20$. Tables II and III show the data for other competition experiments, and Table IV gives a summary of the relative reactivities.

TABLE II

COMPETITIVE OXIDATION OF BENZALDEHYDE AND *p*-TOLUALDEHYDE[a]

Aliquot	Time, min.	Benzaldehyde added, g.	*p*-Tolualdehyde added, g.
1	20.34	2.0150	2.0145
2	74.72	2.0408	1.9967
3	104.72	2.0162	2.0093

Sample[b]	Spec. act. of benzoic acids, μc./g.	Concn. of aldehydes × 10^2
A_1	0.0342	1.44
B_1	.0875	1.57
A_2	.0198	0.663
B_2	.0591	1.03
A_3	.0148	0.606
B_3	.0467	0.816

[a] $[C_6H_5CHO] = 0.025$ *M*, 0.821 μc./g.; $[p\text{-}CH_3C_6H_4CHO] = 0.025$ *M*, 1.74 μc./g.; $[Cr^6] = 0.0337$ *M*, $[HClO_4] = 0.204$ *M*; $[Mg(ClO_4)_2] = 0.065$ *M*, $T = 30.0°$, 91% HOAc. [b] A refers to benzoic acid, B refers to *p*-toluic acid.

As a check on the validity of the equation which was derived above, the series of kinetic equations

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[8] K. B. Wiberg and T. Mill, *J. Am. Chem. Soc.*, **80**, 3022 (1958); G. T. E. Graham and F. H. Westheimer, *ibid.*, **80**, 3030 (1958).

[9] F. H. Westheimer and A. Novick, *J. Chem. Phys.*, **11**, 506 (1943).

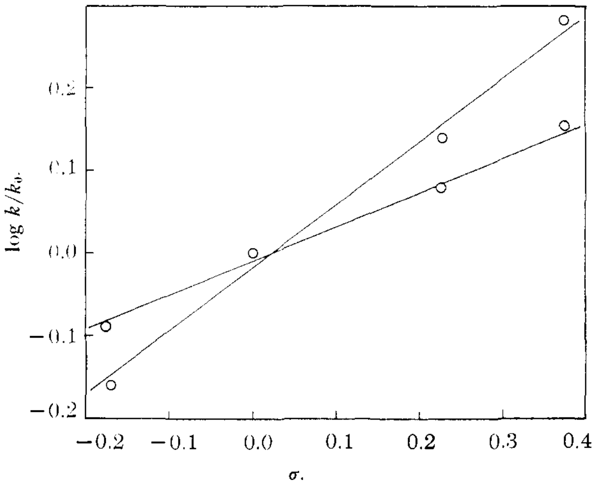

Fig. 2.—Effect of substituents on the rate of oxidation of aromatic aldehydes by chromium(VI) (upper line) and by chromium(V) (lower line). The substituents are p-CH_3, H, p-Cl and m-Cl.

was treated by numerical integration using the relative rates given in Table IV and making the assumption that $k_4 = 10k_1$ and $k_3 = 100k_1$.[10] Plots of log A/A_0 against log B/B_0 using these calculated values gave linear correlations, the slopes of which are given in the third column of Table IV. The good agreement indicates that the equation is satisfactory.

TABLE III

COMPETITIVE OXIDATION OF BENZALDEHYDE AND m-CHLOROBENZALDEHYDE[a]

Aliquot	Time, min.	Benzaldehyde added, g.	m-Chlorobenzaldehyde added, g.
1	12.74	1.8070	2.0215
2	25.95	1.9847	2.0245
3	38.00	2.0531	2.0627

Sample	Spec. act. of benzoic acids, μc./g.	Concn. of aldehydes × 10^2
A_1	0.0434	1.68
B_1	.0596	1.35
A_2	.0326	1.37
B_2	.0457	1.02
A_3	.0269	1.16
B_3	.0326	0.738

[a] $[C_6H_5CHO] = 0.025\ M$, 0.810 μc./g.; $[m\text{-}ClC_6H_4CHO] = 0.025\ M$, 1.20 μc./g.; $[Cr^6] = 0.0326\ M$, $[HClO_4] = 0.204\ M$; $[Mg(ClO_4)_2] = 0.088\ M$, $T = 30.0°$, 91% HOAc.

TABLE IV

SUMMARY OF RELATIVE REACTIVITIES OF AROMATIC ALDEHYDES

Substituent	k/k_0 (over-all) Obsd.	Calcd.[a]	k/k_0 (Cr^6)	k/k_0 (Cr^5)
p-CH_3	0.77	0.76	0.69	0.81
p-Cl	1.26	1.27	1.38	1.20
m-Cl	1.58	1.61	1.91	1.42

[a] Calculated from k/k_0 (Cr^6) and k/k_0 (Cr^5) by numerical integration, making the assumption that $k_0(Cr^6) = 0.1k_0(Cr^5)$.

Plots of the logarithms of the relative rate constants for oxidation by chromium(VI) and chromium(V) against σ are shown in Fig. 2. The value of ρ for chromium(VI) oxidation is 0.77, and that for the intermediate chromium species is 0.45.

Suppose the reaction involved a scheme such as

$$A + Cr^6 \xrightarrow{k_1} P + Cr^4$$

$$B + Cr^6 \xrightarrow{k_2} P + Cr^4$$

$$A + Cr^4 \xrightarrow{k_3} A\cdot + Cr^3$$

$$B + Cr^4 \xrightarrow{k_4} B\cdot + Cr^3$$

$$A + Cr^6 \xrightarrow{k_5} P + Cr^5$$

$$B + Cr^6 \xrightarrow{k_6} P + Cr^5$$

$$A + Cr^5 \xrightarrow{k_7} P + Cr^3$$

$$B + Cr^5 \xrightarrow{k_8} P + Cr^3$$

where A· and B· are the radicals formed by removing a hydrogen atom from A and B, respectively. The steady state approximation may be applied to eliminate the parts of the kinetic expressions which involve A· and B·. There still remain two sets of relative rates, k_3/k_4 and k_7/k_8, to be evaluated. It is difficult to obtain an expression for the relationship between these two ratios of rates, and the available data are not adequate to determine the values of the rate constants under any circumstances.

An estimate may be made for the ratio k_3/k_4 assuming that the effect of substituents will be similar to that observed in the autoxidation of aromatic aldehydes[11] and in other hydrogen atom abstraction reactions.[6,12] Thus ρ was assumed to lie between −0.5 and −1.0.

The set of kinetic equations may now be treated by numerical integration making the assumption that $k_3 = k_7 = 10k_1$. Again, the results are relatively insensitive to the values of these rate constants so long as k_3 and k_7 are greater than k_1. Table V gives values of k_3/k_4 and k_7/k_8 which are in accord with the observed reactivity ratios. Choosing values for k_3/k_4 which correspond to $\rho = -0.5$ and −1.0, plots of the logarithm of the corresponding values of k_7/k_8 (where k_4 and k_3 refer to benzaldehyde) against σ gave reasonable correlations (Fig. 3) with $\rho = +1.6$ and +2.2, respectively.

TABLE V

SUMMARY OF RELATIVE REACTIVITIES FOR THE PROCESS INVOLVING CHROMIUM(IV) AND-(V)

Substituent	k/k_0 (over-all) Obsd.	Calcd.	k/k_0 (Cr^4)	k/k_0 (Cr^5)
p-CH_3	0.77	0.77	1.22[a]	0.45
p-Cl	1.26	1.26	0.77	2.0
m-Cl	1.58	1.58	0.65	3.6
p-CH_3	0.77	0.77	1.48[b]	0.30
p-Cl	1.26	1.26	0.59	2.8
m-Cl	1.58	1.58	0.42	5.9

[a] Based on $\rho(Cr^4) = 0.5$. [b] Based on $\rho(Cr^4) = 1.0$.

In summary, if only chromium(V) is involved after the rate-determining step, the value of ρ for

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[10] The results are not particularly sensitive to the relative values of these rate constants.

[11] C. Walling and E. A. McElhill, *J. Am. Chem. Soc.*, **73**, 2927 (1951).

[12] G. A. Russell, *J. Org. Chem.*, **23**, 1407 (1958).

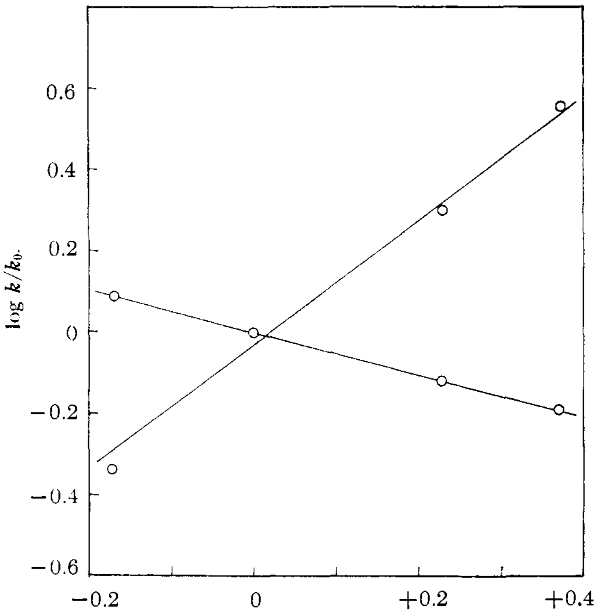

Fig. 3a.—Effect of substituents on the chromium(V) oxidation of benzaldehyde based on ρ for chromium(IV) being −0.5. The lines with negative slope are for chromium(V).

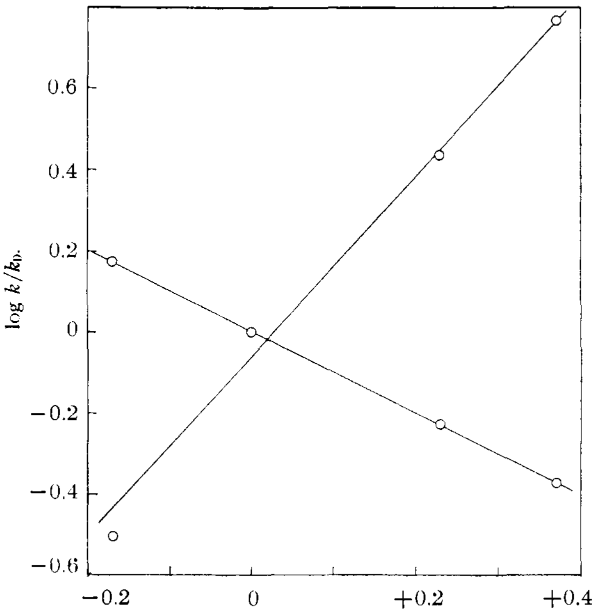

Fig. 3b.—Same plot as Fig. 3a with ρ for chromium(IV) being −1.0.

its reaction is +0.45 whereas that for chromium(VI) is +0.77. If both chromium(IV) and -(V) are involved, and if the reaction by the former is characterized by $\rho = -0.5$, then the corresponding value for the latter is +1.6. Similarly, if the oxidation by chromium(IV) had $\rho = -1.0$, chromium(V) would have $\rho = +2.2$.

The kinetic isotope effect may be determined in the same fashion.[13] A plot of log $[C_6H_5CHO]_t/$

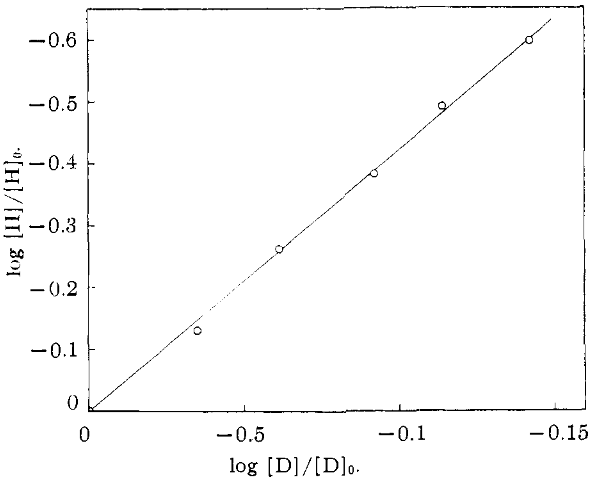

Fig. 4.—Effect of deuterium substitution on the chromic acid oxidation of benzaldehyde.

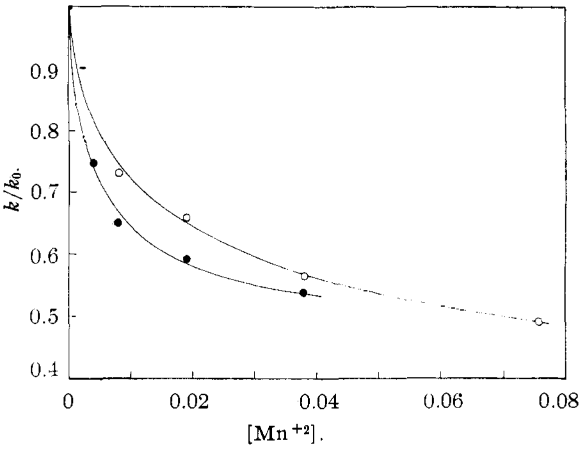

Fig. 5.—Effect of manganous ion concentration on the oxidation of *p*-tolualdehyde (open circles) and *p*-chlorobenzaldehyde (closed circles).

$[C_6H_5CHO]_0$ against log $[C_6H_5CDO]_t/[C_6H_5CDO]_0$ (Fig. 4) gave a slope of 4.17. Correcting for the isotope effect associated with the oxidation by chromium(VI) (4.3),[8] the isotope effect for the later steps was found to be $k_H/k_D = 4.1$.

Another approach to determining the nature of the oxidation by the chromium species of intermediate valence is the study of the induced oxidation of manganous and cerous ions.[2] Neither of the latter ions will react with chromium(VI) at an appreciable rate in reasonably acidic solution. However, either may react with chromium(IV) or -(V). Ceric ion has been found to react readily with benzaldehyde, and thus manganous ion was chosen for this study.

When manganous ion is used for this purpose in aqueous acetic acid solution, it is not permanently oxidized to manganese(III) or -(IV) but, rather, it appears to function by catalyzing the disproportionation of chromium(IV) and -(V).[8] If we now consider mechanisms A and B which were given previously, it can be seen that each involves a net six - electron change. In the presence of manganous ion, all steps after the first will be eliminated, and three chromium(IV) will disproportionate

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[13] The isotope effect for the oxidation of isopropyl alcohol by chromium(V) was determined in this way by L. Kaplan, *J. Am. Chem. Soc.*, **77**, 5469 (1955).

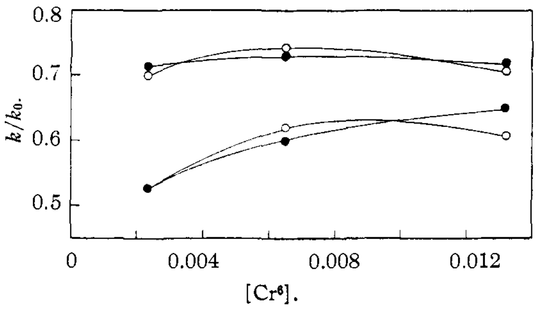


Fig. 6.—Effect of reagent concentrations on the rate reduction by manganous ion. The solid circles refer to a benzaldehyde concentration of 0.1 *M*, and the open circles, 0.06 *M*. The upper lines refer to a manganous ion concentration of 0.003 *M*, and the lower two, 0.019 *M*.

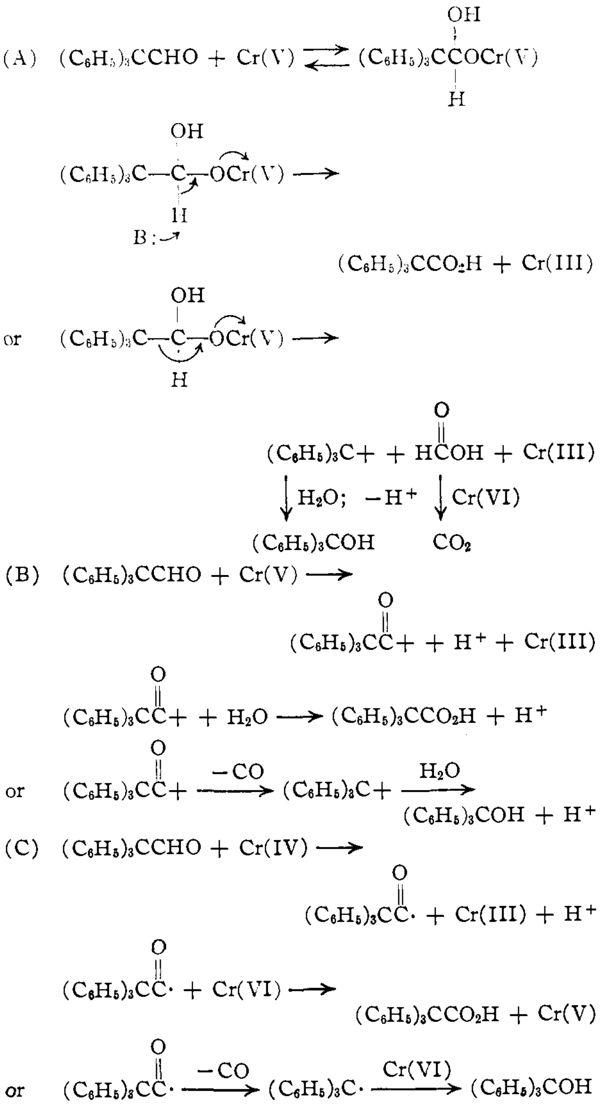
to give one chromium(VI) and two chromium(III). This is a net two-electron change, and the addition of manganous ion should then give a rate of reaction one-third that observed in its absence. The effect of manganous ion on the oxidation of *p*-tolualdehyde is shown in Fig. 5, and it can be seen that the rate is reduced to somewhat below one-half of the original rate.

Suppose the concentration of manganous ion were such that maximum retardation was not obtained. If mechanism A were correct, manganous ion and chromium(VI) could compete for chromium(IV). Also, manganous ion and aldehyde could compete for chromium(V). At a constant manganous ion concentration, the rate of reaction should be a function of chromium(VI) or aldehyde concentration or both. If, mechanism B were correct, the competition should be between manganous ion and the aldehyde for chromium(IV) and at a constant manganous ion concentration, the rate of reaction should be a function of the aldehyde concentration. In this case there should not be a dependence on the concentration of chromium(VI). Plots showing the necessary data are given in Fig. 6.

It can be seen that there is not a marked effect of concentration of either chromium(VI) or *p*-chlorobenzaldehyde on the rate retardation. The obvious conclusion is that the nature of the induced oxidation is not well enough understood at the present time to permit an interpretation of these data. It is possible that the manganese(III) or -(IV) which is present at a steady-state concentration may oxidize the aldehyde, and it is also possible that the reactivity of chromium(V) may be a function of the chromium(VI) concentration as a result of the formation of a complex between these species.[5]

A comparison of the effect of manganous ion the oxidation of *p*-chlorobenzaldehyde and *p*-tolualdehyde is of interest (Fig. 5). It can be seen that at a low manganous ion concentration, the larger rate reduction is obtained with *p*-chlorobenzaldehyde, and this suggests that *p*-tolualdehyde is more readily oxidized by some species which is present, than is *p*-chlorobenzaldehyde. The reactivity toward chromium(V) is the opposite with the latter being the more reactive. Thus, either chromium(IV) or manganese(III) or -(IV) effects oxidation of the aldehyde and this reaction has a negative ρ.

Still another method for studying the reactions of the chromium species of intermediate valence involves the use of a compound which will give different products for different reaction paths. Among aldehydes, one compound of this type might be triphenylacetaldehyde. Some of the possible modes of reaction are



(A) $$(C_6H_5)_3CCHO + Cr(V) \rightleftharpoons (C_6H_5)_3\overset{OH}{\underset{H}{C}}OCr(V)$$

$$(C_6H_5)_3C{-}\overset{OH}{\underset{\substack{H\\ B:}}{C}}{-}OCr(V) \longrightarrow$$

$$(C_6H_5)_3CCO_2H + Cr(III)$$

or $$(C_6H_5)_3C{-}\overset{OH}{\underset{H}{C}}{-}OCr(V) \longrightarrow$$

$$\begin{array}{ccc} (C_6H_5)_3C+ & + \; H\overset{\overset{O}{\|}}{C}OH & + \; Cr(III) \\ \downarrow H_2O; \; -H^+ & \downarrow Cr(VI) & \\ (C_6H_5)_3COH & CO_2 & \end{array}$$

(B) $$(C_6H_5)_3CCHO + Cr(V) \longrightarrow (C_6H_5)_3C\overset{\overset{O}{\|}}{C}+ + H^+ + Cr(III)$$

$$(C_6H_5)_3C\overset{\overset{O}{\|}}{C}+ + H_2O \longrightarrow (C_6H_5)_3CCO_2H + H^+$$

or $$(C_6H_5)_3C\overset{\overset{O}{\|}}{C}+ \xrightarrow{-CO} (C_6H_5)_3C+ \xrightarrow{H_2O} (C_6H_5)_3COH + H^+$$

(C) $$(C_6H_5)_3CCHO + Cr(IV) \longrightarrow (C_6H_5)_3C\overset{\overset{O}{\|}}{C}\cdot + Cr(III) + H^+$$

$$(C_6H_5)_3C\overset{\overset{O}{\|}}{C}\cdot + Cr(VI) \longrightarrow (C_6H_5)_3CCO_2H + Cr(V)$$

or $$(C_6H_5)_3C\overset{\overset{O}{\|}}{C}\cdot \xrightarrow{-CO} (C_6H_5)_3C\cdot \xrightarrow{Cr(VI)} (C_6H_5)_3COH$$

Oxidation by any one of the three paths may lead to triphenylacetic acid, and if this were the only product, no information would be gained. However, if triphenylcarbinol is also formed, one may look for carbon monoxide or carbon dioxide as the other product. The former cannot be formed *via* path A, and the latter cannot be formed by paths B or C.[14]

In order to have a better idea of how the reaction might proceed, the oxidation by several other oxidants was first studied. The permanganate oxidation of aldehydes in neutral solution almost certainly involves an ester mechanism.[15] Oxida-

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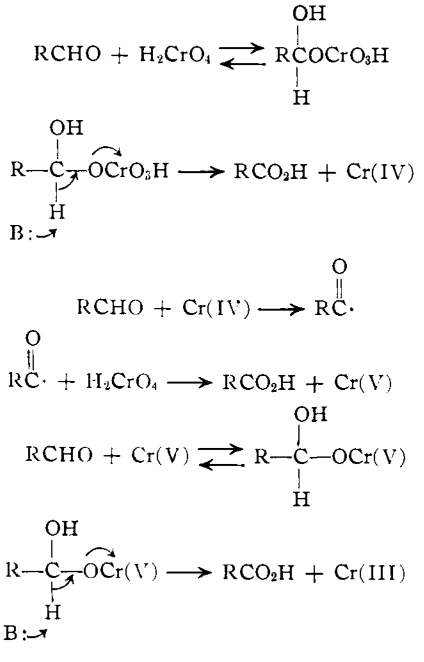
[14] Carbon monoxide is not oxidized by chromic acid under the reaction conditions.

tion of triphenylacetaldehyde by permanganate gave triphenylacetic acid (95%) and no triphenylcarbinol.[16] The oxidation of aldehydes by chromyl acetate[17] and by ceric ion[17] appears to involve a hydrogen abstraction, and in this case triphenylcarbinol and carbon monoxide were the only products, and no triphenylacetic acid could be isolated.

The chromic acid oxidation of triphenylacetaldehyde in aqueous acetic acid solution gave as products, triphenylacetic acid (61%), triphenylcarbinol (24%) and a gas consisting of 82 mole % carbon monoxide and 18 mole % carbon dioxide. It must be admitted that triphenylacetaldehyde may be a special case and may react by a different mechanism than other aldehydes. However, the formation of about one-third triphenylcarbinol and carbon monoxide indicates that at least one-third of the reaction proceeds *via* a process which does not involve an ester intermediate. The formation of about two-thirds triphenylacetic acid suggests that the ester mechanism may account for two-thirds of the reaction, particularly in view of the results obtained with the other oxidizing agents.

It is clear that the data are not adequate to permit an unequivocal decision between the possible reaction paths for the oxidation of benzaldehyde. The mechanistic scheme which seems to best fit the data is



$$\mathrm{RCHO} + \mathrm{H_2CrO_4} \rightleftarrows \mathrm{R}\overset{\mathrm{OH}}{\underset{\mathrm{H}}{\mathrm{C}}}\mathrm{OCrO_3H} \tag{1}$$

$$\mathrm{R{-}}\overset{\mathrm{OH}}{\underset{\mathrm{H}}{\mathrm{C}}}\mathrm{{-}OCrO_3H} \longrightarrow \mathrm{RCO_2H} + \mathrm{Cr(IV)} \quad \mathrm{B{:}} \tag{2}$$

$$\mathrm{RCHO} + \mathrm{Cr(IV)} \longrightarrow \mathrm{R}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\cdot \tag{3}$$

$$\mathrm{R}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\cdot + \mathrm{H_2CrO_4} \longrightarrow \mathrm{RCO_2H} + \mathrm{Cr(V)} \tag{4}$$

$$\mathrm{RCHO} + \mathrm{Cr(V)} \rightleftarrows \mathrm{R{-}}\overset{\mathrm{OH}}{\underset{\mathrm{H}}{\mathrm{C}}}\mathrm{{-}OCr(V)} \tag{5}$$

$$\mathrm{R{-}}\overset{\mathrm{OH}}{\underset{\mathrm{H}}{\mathrm{C}}}\mathrm{{-}OCr(V)} \longrightarrow \mathrm{RCO_2H} + \mathrm{Cr(III)} \quad \mathrm{B{:}} \tag{6}$$

The evidence for steps 1 and 2 has been presented previously.[6,8] Steps 5 and 6 are written as involving chromium(V) and an ester mechanism for the following reasons: chromium(V) must be involved as an intermediate regardless of which sequence of oxidation steps is postulated; the oxidation by chromium(V) has a small positive value of ρ if it is the only species involved after the rate-determining step, and probably has a moderately large positive value of ρ if chromium(IV) is also involved. If a hydride abstraction mechanism were operative, one would expect a value of ρ significantly more negative than that for the oxidation by chromium(VI).[6] Finally, steps 5 and 6 along with 1 and 2 would lead to the formation of 66% triphenylacetic acid from triphenylacetaldehyde.

The oxidation by chromium(V), if it proceeds *via* an ester mechanism, should have a significantly more positive value of ρ than for the oxidation by chromium(VI). It appears that the activated complex for the oxidation by chromium(VI) is well along the reaction coördinate so that it partakes of the character of the products.[6] The reaction *via* chromium(V) should have a lower activation energy than that involving chromium(VI) since the former reaction is the more rapid of the two. Thus the activated complex should be less far along the reaction coördinate and should partake of the character of the reactants. In this case, the argument that electron-withdrawing groups should accelerate the decomposition of the ester intermediate[18] will apply, leading to a positive value of ρ.

In support of this hypothesis, it might be mentioned that whereas the oxidation of benzhydrol by chromium(VI) gives a ρ of -0.9, the value for the oxidation by chromium(V) is approximately $+1.8$.[19] Similarly, electron-withdrawing groups accelerate the dehydrohalogenation of β-phenylethyl halides ($\rho = +2.5$).[20]

If one makes the assumption that only chromium(V) is involved after the rate-determining step one finds that the value of ρ for its reaction is somewhat *less* positive than that for chromium(VI). This appears unreasonable. However, if steps 3 and 4 are included, they will make the value of ρ for the chromium(V) oxidation be between $+1.6$ and $+2.2$, which is quite reasonable. Furthermore, these steps will lead to the formation of 33% triphenylcarbinol and carbon monoxide from triphenylacetaldehyde, and will account for the difference in the rate retardation by manganous ion between *p*-tolualdehyde and *p*-chlorobenzaldehyde. A one-electron oxidation of an aldehyde by chromium(IV) is reasonable in view of the ease of hydrogen atom abstraction from this type of compound.

It should be emphasized that we do not consider the above mechanistic hypothesis to be firmly established by our results. However, it does serve to correlate the data and will serve as a starting point for further studies.

Experimental[21]

Reagents.—The solvent used for all the experiments was purified 91% (by weight) acetic acid–water.[8] All the solid inorganic compounds were reagent grade and were dehydrated prior to making the solutions. The chromium(VI) solutions were prepared from sodium dichromate. The stock perchloric acid solution in 91% acetic acid was pre-

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[15] K. B. Wiberg and R. Stewart, *J. Am. Chem. Soc.*, **77**, 1786 (1955).

[16] This experiment was performed by Dr. J. Cawley.

[17] Unpublished results of P. Lepse and W. H. Richardson of these laboratories.

[18] J. Rocek, *Tetrahedron Letters*, **No. 5**, 1 (1959).

[19] Unpublished results of W. Giddings and J. Cawley of these laboratories.

[20] S. J. Cristol, *J. Am. Chem. Soc.*, **67**, 1494 (1945); S. J. Cristol, N. L. Hause, A. J. Quant, H. W. Miller, K. R. Eilar and J. S. Meek, *ibid.*, **74**, 3333 (1952).

[21] All melting points are corrected unless otherwise indicated. All boiling points are uncorrected.

pared from 71% reagent grade perchloric acid as previously described.[8]

p-Tolualdehyde and benzaldehyde were purified immediately before use by distillation under a nitrogen atmosphere. Purification of *p*-chlorobenzaldehyde was accomplished by recrystallization from an ethanol–water mixture followed by sublimation, m.p. 46.5–47.5°. Benzaldehyde-*d*, b.p. 179–180°, was prepared from benzil (78%) by the procedure previously described.[22]

Benzaldehyde-C^{14}.—Benzaldehyde-C^{14}, *p*-chlorobenzaldehyde-C^{14} and *p*-tolualdehyde-C^{14} were prepared from the corresponding acids *via* the Rosenmund reduction.[23] The *m*-chlorobenzaldehyde-C^{14} was prepared by the reduction of the acid chloride with tri-*t*-butoxylithium aluminum hydride.[24]

Competitive Oxidation of Substituted Benzaldehydes.—The oxidations were carried out in a 200-ml. flask equipped with a tube for withdrawing aliquots and a nitrogen inlet tube. The temperature was controlled by a Sargent constant temperature water-bath. All measurements were made at 30.00°. Three solutions were prepared in 50-ml. volumetric flasks. One solution contained sodium dichromate, another had perchloric acid and magnesium perchlorate and the last solution contained equimolar concentrations of the carbon-14 aldehydes. In all cases the solvent was 91% acetic acid. After thermally equilibrating the solutions for 0.5 hr., they were mixed in the reaction flask and 50-ml. aliquots were withdrawn at recorded times. Each aliquot was quenched by adding it to 20 ml. of 0.2 *M* sodium arsenite in 2 *M* hydrochloric acid. To each aliquot was added a weighed amount of benzaldehyde-C^{12} and substituted benzaldehyde-C^{12}.

The aliquots were worked up in the following manner. First, 20-ml. of water was added and the solution was extracted with three 25-ml. portions of methylene chloride. The combined methylene chloride extracts were washed with three 30-ml. portions of 10% sodium carbonate solution followed by 10 ml. of water. After drying over magnesium sulfate, the methylene chloride extracts were concentrated using a rotary evaporator. The mixture of aldehydes was then passed through either a Beckman GC-2 or an Aerograph vapor phase chromatograph using a silicone column at 150–160°. The *p*-methyl- and *p*-chlorobenzaldehydes were then oxidized by passing air over the aldehyde and irradiating the reaction mixture with a 140 watt Hanovia ultraviolet light source. An aqueous potassium permanganate oxidation was used to convert *m*-chlorobenzaldehyde to its acid. Benzaldehyde was oxidized by both methods. All the acids were finally purified by sublimation. Recrystallization from carbon tetrachloride and carbon tetrachloride–acetone was used to purify *p*-toluic acid and *p*-chlorobenzoic acid, respectively, before sublimation. The following melting points were observed: benzoic acid, 122–122.5°; *m*-chlorobenzoic acid, 157–158°; *p*-toluic acid, 177–178°; and *p*-chlorobenzoic acid, 239–240° (uncor.). The carbon-14 content was determined using a liquid scintillation counter with an independent determination of counting efficiency for each sample.[25]

Kinetic Measurements for Manganese(II) Experiments.—The kinetics were measured titrimetrically by the method of Wiberg and Mill.[8] The manganese(II) perchlorate solution was prepared by adding a calculated amount of 0.900 *M* perchloric acid in 91% acetic acid to a weighed quantity of manganese(II) acetate. The resulting solution was then diluted with 91% acetic acid to the desired concentration.

Kinetic Isotope Effect.—The general procedure was the same as that described for the competitive oxidation experiments, with the following exceptions. Aliquots of 25.0 ml. were withdrawn, with the exception of the last aliquot which was 50 ml., and quenched with 20 ml. of 0.2 *M* sodium arsenite in 2 *M* hydrochloric acid containing 0.2 mg. of *t*-butylcatechol. The aliquots were extracted with *n*-pentane and the combined extracts were washed with 10% sodium carbonate solution. An additional 0.2 mg. of *t*-butylcatechol was added, the aliquots were concentrated to remove *n*-pentane and the mass spectrum of each aliquot was measured. The ratios of [benzaldehyde-d_0]/[benzaldehyde-d_1] = ([H]/[D]) were calculated from eq. 1 for each aliquot, where all the concentrations are relative. The relative concentrations of $C_6H_5\overset{12}{C}HO$ and $C_6H_5\overset{13}{C}DO$ could be determined directly from the mass spectrum.

$$\frac{[H]}{[D]} = \frac{[C_6H_5\overset{12}{C}HO] + [C_6H_5\overset{13}{C}HO]}{[C_6H_5\overset{12}{C}DO] + [C_6H_5\overset{13}{C}DO]} \qquad (1)$$

Since $C_6H_5\overset{13}{C}HO$ and $C_6H_5\overset{12}{C}DO$ have the same mass number, two simultaneous equations were used to determine the relative concentrations of these two aldehydes. The equations are given below and I is the intensity at mass number 107. In a separate kinetic measurement, the specific rate constant was found to be 3.52×10^{-3} l. mole^{-1} sec.$^{-1}$ at 30.00° for identical concentrations of reactants as in the mass spectral determinations. The concentrations used in both runs were: $[C_6H_5CHO] = [C_6H_5CDO] = 0.0244$ *M*, $[Cr^6] = 0.0326$ *M*, $[HClO_4] = 0.024$ *M* and $[NaClO_4] = 0.060$ *M*. With the aid of eq. 4 and the above rate constant, the combined concentrations of unreacted aldehydes were determined for the times at which aliquots were withdrawn in the competition run. In eq. 4, x_t and x_0 equal the combined aldehyde concentrations at time t and at $t = 0$, respectively. With the ratios of (benzaldehyde-d_0)/(benzaldehyde-d_1) and the values of x_t for each aliquot at these times, the concentrations of benzaldehyde-d_0 and benzaldehyde-d_1 could be determined for the aliquots.

$$[C_6H_5\overset{13}{C}HO] + [C_6H_5\overset{12}{C}DO] = I \qquad (2)$$

$$\frac{[C_6H_5\overset{12}{C}HO]}{[C_6H_5\overset{13}{C}HO]} = \frac{[C_6H_5\overset{12}{C}DO]}{[C_6H_5\overset{13}{C}DO]} \qquad (3)$$

$$\left[\frac{1}{x_t} - \frac{1}{x_0}\right] = k_2t \qquad (4)$$

Chromic Acid Oxidation of Triphenylacetaldehyde.—A solution of 26.1 ml. of 0.0940 *M* (in Cr^6) sodium dichromate and 12.0 ml. of 0.900 *M* perchloric acid was prepared in 91% acetic acid solution. A solution of triphenylacetaldehyde was prepared from 1.00 g. of triphenylacetaldehyde and 50 ml. of 91% acetic acid. Some warming was required to dissolve the triphenylacetaldehyde. The two solutions were mixed and allowed to react under a nitrogen atmosphere for 18 hr. Evolution of a gas was noted.

The dark green reaction mixture was filtered and the white crystals of triphenylacetic acid (0.31 g.), m.p. 258–260° dec. (uncor.) (lit.[26] m.p. 264–265°), were washed with 91% acetic acid. The filtrate was extracted with four 50-ml. portions of methylene chloride, after adding 40 ml. of water. The combined organic extracts were washed with three 30-ml. portions of water to remove acetic acid. The use of base was avoided, since triphenylacetaldehyde is known to react with base. The methylene chloride extract was dried over magnesium sulfate and concentrated using a rotary evaporator. About 20 ml. of cyclohexane was added and the mixture was heated to reflux for a few minutes. The suspension was filtered upon cooling and an additional 0.28 g. of triphenylacetic acid, m.p. 258–260° dec. (uncor.), was obtained. Another 0.06 g. of triphenylacetic acid, with the same melting point, was produced upon slight concentration of the filtrate. The total yield of triphenylacetic acid was 0.65 g. (61% of theory).

Upon considerable concentration of the above filtrate another crop of crystals was precipitated. After recrystallization from an ether–*n*-hexane mixture, 0.23 g. (24% of theory), m.p. 160–162°, of triphenylcarbinol was obtained. A mixed melting point with an authentic sample showed no depression.

To determine the composition of the gas which was evolved in the oxidation of triphenylacetaldehyde, the reaction was carried out in an evacuated two-armed cell. Two solutions were prepared, one solution for each arm of the reaction cell.

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[22] K. B. Wiberg, *J. Am. Chem. Soc.*, **76**, 5371 (1954).

[23] D. Jerchel, H. Becker and K. Schmeiser, *Z. Naturforsch.*, **8b**, 294 (1953).

[24] H. C. Brown and B. C. S. Rao, *J. Am. Chem. Soc.*, **80**, 5377 (1958).

[25] The analyses were performed by the New England Nuclear Assay Co., Boston Mass.

[26] P. G. Scholefield, S. T. Bowden and W. J. Jones, *J. Soc. Chem. Ind.*, **66**, 447 (1947).

TABLE VI

MASS SPECTROGRAPHIC DETERMINATION OF CARBON MONOXIDE AND CARBON DIOXIDE FOR THE CHROMIC ACID OXIDATION OF TRIPHENYLACETALDEHYDE

Sample[a]	Peak 28	Peak 32	Peak 44
Air	1527	166	4.5
Reaction product	2562	8.4	584
Reaction product (cor. for air present)	2485	0	584
CO	3010	...	....
CO_2	..	...	3440

[a] All corrected to pressure = 35.1 μ; background subtracted from all samples.

The arms of the reactions cell were placed in a Dry Ice–acetone-bath and the system was evacuated by a mercury diffusion pump. The cell was allowed to warm to room temperature, the contents were again frozen, and the cell was re-evacuated. The solutions were mixed by inverting the reaction cell after warming to room temperature. After allowing the reaction to proceed for 17 hr., the reaction mixture was frozen in a Dry Ice–acetone-bath and the gas above the reaction mixture was analyzed mass spectrometrically. One solution contained 4.00 ml. of 0.0940 M (in Cr^6) of sodium dichromate plus 2.00 ml. of 0.900 M perchloric acid both in 91% acetic acid. The other solution contained 0.1535 g. (0.564 mmole) of triphenylacetaldehyde in 10.0 ml. of 91% acetic acid solution. The final concentrations were: $((C_6H_5)_3CCHO) = 0.0353\ M$, $(Cr^6) = 0.0235\ M$ and $(HClO_4) = 0.113\ M$. The mass spectral data are given in Table VI. The mole percentages of carbon monoxide (82%) and carbon dioxide (17%) were calculated from these data.

Triphenylacetic Acid in Chromic Acid.—A mixture of 0.100 g. (0.348 mmole) of triphenylacetic acid, 6.00 ml. of 0.0940 M (in Cr^6) of sodium dichromate and 3.00 ml. of 0.900 M perchloric acid in a total of 20.0 ml. of 91% acetic acid was prepared. The mixture was poured into 30 ml. of 0.2 M sodium arsenite solution in 2 M hydrochloric acid after 48 hr. at 30°.

The mixture was filtered and 0.04 g. of triphenylacetic acid, m.p. 258–260° dec. (uncor.) (lit.[26] m.p. 264–265°) was collected. The filtrate was extracted with three 50-ml. portions of methylene chloride and the combined methylene chloride extracts were washed with two 10-ml. portions of water. Concentration of the methylene chloride extract, after drying over magnesium sulfate, gave 0.05 g. of triphenylacetic acid, m.p. 258–260° dec. (uncor.). The total amount of recovered triphenylacetic acid was 0.09 g. (90% recovery).

Carbon Monoxide in Chromic Acid.—Carbon monoxide (Matheson C.P.) was bubbled through 50.0 ml. of 91% acetic acid solution which was 0.0302 M in chromium(VI) and 0.126 M in perchloric acid. Aliquots (2.00 ml.) were analyzed titrimetrically by a method previously used by Wiberg and Mill.[8] No change in titer was noted over a 100-hour period.

Calculation of Concentrations by Numerical Integration.—The concentrations were determined from the differential equations appropriate to the system and the rate constants given in the results section using fourth order Runge–Kutta numerical integration.[27] An IBM-709 computer was used in performing the numerical calculations. Independent checks of this method indicate that the results will be in error by less than 0.1%.

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[27] W. E. Milne, "Numerical Calculus," Princeton University Press, Princeton, N. J., 1949.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF WISCONSIN, MADISON 6, WIS.]

Homologation of the Triphenylmethyl Cation

BY H. W. WHITLOCK, JR.

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Homologation of the triphenylmethyl cation by diazomethane affords, as end products, triphenylethylene and 1,2,3-triphenylpropene. Homologation by phenyldiazomethane affords stilbene and tetraphenylethylene. Homologation by diphenyldiazomethane affords tetraphenylethylene, the triphenylmethyl cation serving as a catalyst. The results are interpreted in terms of simple carbonium ion behavior.

Introduction

Reactions of diazo compounds may be best interpreted in light of resonance structure **1**.

$$R\overset{-}{C}_2\text{–}N_2\text{–}n \overset{n^-}{\leftrightarrows} \underset{1}{R_2\overset{-}{C}\text{–}\overset{+}{N}_2} \overset{E^+}{\rightleftarrows} R_2CE\text{–}\overset{+}{N}_2$$

In accordance with this structure, reactions of diazo compounds with electrophiles (E^+) proceed *via* electrophile–carbon bond formation. Similarly, reactions with nucleophiles (n^-) proceed *via* nucleophile–nitrogen bond formation. Many examples of this ambivalent character of diazo compounds are found in the literature—reactions with metal salts, acid chlorides, α,β-unsaturated carbonyl and nitro compounds, carboxylic and non-carboxylic acids, simple carbonyl groups, Grignard reagents, diazonium salts and even other diazo compounds[1] being known.

As set forth in a previous communication,[2] we have now extended this list by proposing the reaction between diazo compounds and carbonium ions. The proposed reaction involves formation of a primary adduct **3** followed by rapid loss of nitrogen to afford a new carbonium ion **4**. The subsequent pathways of reaction which are open to **4** then will be determined by the nature of R and R′, Wagner–Meerwein rearrangements followed by either proton loss or reaction with a nucleophile being most likely.[3] That the reaction as formulated is feasible has been already demonstrated by the one-step preparation of dibenz[b,f]oxepin, dibenzo[b,f]thiepin and N-methyldibenz[b,f]azepin from the heterocyclic xanthylium, thiaxanthylium and N-methylacridinium cations, respectively.[2] Another example of the generality of this reaction is

$$\underset{2}{R_3\overset{+}{C}} + R_2'CN_2 \longrightarrow \underset{3}{R_3C\text{—}CR_2'\overset{+}{N}_2} \longrightarrow$$
$$\underset{4}{R_3C\text{—}\overset{+}{C}R_2'} \longrightarrow \text{products}$$

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[1] R. Huisgen and R. Fleischmann, *Ann.*, **623**, 47 (1959).

[2] H. W. Whitlock, Jr., *Tetrahedron Letters*, 593 (1961).

[3] (a) A. Streitwieser, Jr., *J. Org. Chem.*, **22**, 861 (1957); (b) B. M. Benjamin, P. Wilder, Jr., and C. J. Collins, *J. Am. Chem. Soc.*, **83**, 3654 (1961).